Nd$_2$Ba$_2$CaCu$_{2-x}$Zn$_x$Ti$_3$O$_{14}$: a new family of tunable dielectric oxides showing a compositionally controlled tetragonal to cubic transition

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**Abstract**

Oxides of the formula Nd$_2$Ba$_2$Ca$_{2-x}$Zn$_x$Ti$_3$O$_{14}$ (x = 0.0, 0.5, 1.0, 1.5, 2.0) have been successfully prepared by high temperature ceramic route at 1025 °C, as well as by the low temperature citrate precursor route at 800 °C. The copper-rich compounds obtained by the ceramic route (x = 0-1.0) are found to have a tetragonal structure, with the $a$ and $c$ parameters increasing with zinc substitution, from $a = 3.913(8)$ Å and $c = 19.630(1)$ Å for x = 0, to $a = 3.925(1)$ Å and $c = 19.640(1)$ Å for x = 1. The tetragonal distortion decreases with increase in zinc substitution and the oxides with x > 1.5 were found to crystallize in the cubic structure with $a = 3.933(2)$ Å and $a = 3.937(1)$ Å for the x = 1.5 and two compositions, respectively. The entire range of oxides (0 < x < 2) could be obtained as pure phases at 800 °C and crystallize in the cubic structure when prepared by the citrate precursor route. The room temperature dielectric constant ($\varepsilon$) at 100 kHz varies from 8 for the pure Cu composition and increased to 59 for the pure Zn analog. The dielectric constant depends on the synthetic route—the pure Zn compound Nd$_2$Ba$_2$CaZn$_2$Ti$_3$O$_{14}$ gave much lower dielectric constant ($\varepsilon$) of 23 at 100 kHz when prepared by the citrate precursor method ($\varepsilon = 59$, solid state route).

**Keywords:** A. Ceramic; C. Scanning electron microscopy

1. Introduction

Complex perovskite related oxides have been of great importance since a number of materials exhibiting a wide range of properties ranging from insulators to superconductors, magnetic and dielectric materials can be synthesized based on the perovskite structure. The simple perovskite structure (ABO$_3$) serves as the building block for a large number of intergrowth or ordered structures
The discovery of a large number of high $T_c$ copper oxide superconductors [4] which show ordered perovskite-related structures has led to the design of several new families of complex metal oxides like Gd$_2$Ba$_2$Ti$_2$Cu$_2$O$_{11}$ [5], La$_2$Ba$_2$Sn$_2$Cu$_2$O$_{11}$ [6] that are non-superconducting and are also based on the ordered perovskite structures. The rare earth based copper titanates of the formula Ln$_2$Ba$_2$CaCu$_2$Ti$_3$O$_{14}$ (Ln = La, Nd, Sm, Eu, Gd, etc.) have been synthesized recently [7,8]. The structure of these oxides can be conceived of as the intergrowth of three TiO$_6$ (octahedral) and two CuO$_5$ (square-pyramidal) layers in a repeat unit to form a ordered tetragonal structure, except in the case of lanthanum where it gives a disordered cubic structure.

Recently, we have reported [9,10] the structure of Ln$_2$Ba$_2$CaZn$_2$Ti$_3$O$_{14}$ (Ln = La, Nd, Pr) where we have replaced the Cu ion with Zn. Our aim was to synthesize materials with d$^{10}$ ions so as to obtain new materials with useful dielectric properties. Detailed structural analysis of the oxide Nd$_2$Ba$_2$CaZn$_2$Ti$_3$O$_{14}$ using X-ray, neutron and electron diffraction show that these oxides crystallized in the disordered (cubic) perovskite structure (space group $Pm3m$). There was no evidence of any form of ordering in these oxides. This was unlike their copper-based analogs reported earlier [8]. The formula of Nd$_2$Ba$_2$CaZn$_2$Ti$_3$O$_{14.4}$ can thus be represented as (Nd$_0.4$Ba$_0.4$Ca$_0.2$)(Zn$_0.4$Ti$_0.6$)O$_{2.9}$ where the A and B sites of the cubic perovskite structure (ABO$_3$) are occupied by more than one type of atom. The dielectric properties of the above Zn bases oxides were found to be interesting with dielectric constant (e) close to 60. However, there were no such studies on the Cu analogs. We, therefore, synthesized the solid solution Nd$_2$Ba$_2$CaCu$_2$Zn$_x$Ti$_3$O$_{14}$, in an attempt to fully understand the effect of the transition metal ion (Cu) on the dielectric properties of the above perovskite like oxides. In this paper we report the synthesis and X-ray diffraction studies of this family of oxides synthesized by the ceramic route and the citrate precursor route. The citrate precursor route has been used earlier for the synthesis of a variety of oxides [11-14] where it has been found to be useful to obtain monophasic oxides at reasonably low temperatures of 800-900 °C. We also report the dielectric properties of the above compounds as a function of frequency and temperature.

2. Experimental

Nd$_2$Ba$_2$CaCu$_2$Zn$_x$Ti$_3$O$_{14}$ type of oxides were prepared by two methods, namely the ceramic method and the polymeric citrate precursor method. In the ceramic method, stoichiometric amounts of Nd$_2$O$_3$ (CDH, 99.9%), TiO$_2$ (CDH, 99.99%), CaCO$_3$ (Merck, 98.5%), BaCO$_3$ (Loba Chemie, 99%), ZnO (CDH, 99.5%), and CuO (Loba Chemie, 99%) were taken. Nd$_2$O$_3$ was dried at 900 °C for 6 h before weighing, while the other reactants were dried at 150 °C. The oxides and carbonates were thoroughly mixed in an agate mortar and loaded in alumina boats. The mixed powders were heated in an electrical muffle furnace at 900 °C for 12 h followed by further heating at 1025 °C for 48 h with two intermittent grindings. In some cases (Nd$_2$Ba$_2$CaZn$_2$Ti$_3$O$_{14}$), heating upto 1200 °C was carried out in an attempt to obtain pure a phase. After heating, the powder was cooled to room temperature, homogenized, and mixed with polyvinyl alcohol (PVA) and compacted into pellets at a pressure of 4 tonnes. The pellets were then sintered at 1200 °C for 14 h.

In the polymeric citrate precursor method, citric acid (Qualigens, SQ grade 99.5%), previously dried at 100 °C for 6 h, was mixed with ethylene glycol (Qualigens, SQ grade) and titanium tetraisopropoxide (Acros, 98% p) in the ratio of 10:40:1 with continuous stirring on a magnetic stirrer. After a clear solution was formed at room temperature, the mixture of oxides and carbonates of
metal ions (of the same purity as those used in the ceramic method), except for TiO₂, were added slowly in stoichiometric amount with continuous stirring. The temperature was increased to 100 °C so as to dissolve the entire amounts of solids added. The solution was then placed in the oven at 135 °C when the polymerization sets in. The polymer was charred at 300 °C for 2 h followed by heating at 500 °C for 20 h and 800 °C for 8 h in an electrical muffle furnace. The product was treated with PVA and compacted into pellets at a pressure of 4 tonnes and sintered at a temperature of 1000 °C for 20 h.

Powder X-ray diffraction patterns were taken after each heating step with a Bruker D8 Advance X-ray diffractometer using a step size of 0.05 and a step time of 1 s. The lattice parameters were obtained by a least squares fit to the observed d-values. Scanning electron micrographs (SEM) were obtained on a Cambridge Stereoscan 360 electron microscope on pellets sintered at 1200 °C. The dielectric constant of the oxides made by the ceramic route was measured on pellets sintered at 1200 °C and those prepared by the citrate route were sintered at 1000 °C. For the dielectric properties, all the disks were coated with silver and measured using a HP 4284L LCR meter in the frequency range of 50-500 kHz. Temperature variation studies of the dielectric constant and dielectric loss was carried out in the range of 50-300 °C. Density of the sintered disks was obtained using the Archimedes’ principle and was found to vary from 93 to 95% of the theoretical density for the samples synthesized by the solid state route, and around 92% for those synthesized by the citrate route.

3. Results and discussion

X-ray diffraction patterns of the samples prepared by the solid state route by heating at 1025 °C for 48 h show that the oxides belonging to the solid solutions of the type Nd₂Ba₂CaCu₂₋ₓZnₓTi₃O₁₄ were successfully prepared. The X-ray patterns show the formation of a perovskite phase along with minor amount of ZnO (5%) and Nd₂O₃ (3%) in case of compounds where i^0. However, the samples sintered at 1200 °C for 14 h gave a pure phase (Fig. 1). It is seen that in case of the copper rich

![Fig. 1. Powder X-ray diffraction pattern of Nd₂Ba₂CaCu₂₋ₓZnₓTi₃O₁₄ prepared by the ceramic route after sintering at 1200 °C: (a) x = 0, (b) x = 0.5, (c) x = 1.0, (d) x = 1.5, and (e) x = 2.0.](image-url)
Table 1  
The lattice parameters of Nd$_2$Ba$_2$CaCu$_{2-x}$Zn$_x$Ti$_3$O$_{14}$ for different values of $x$ prepared by the ceramic route  

<table>
<thead>
<tr>
<th>Composition ($x$)</th>
<th>Lattice parameters (Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$</td>
<td>$c$</td>
</tr>
<tr>
<td>0.0</td>
<td>3.913(8)</td>
<td>19.63(1)</td>
</tr>
<tr>
<td>0.5</td>
<td>3.920(1)</td>
<td>19.640(8)</td>
</tr>
<tr>
<td>1.0</td>
<td>3.925(1)</td>
<td>19.64(1)</td>
</tr>
<tr>
<td>1.5</td>
<td>3.93(2)</td>
<td>–</td>
</tr>
<tr>
<td>2.0</td>
<td>3.937(1)$^a$</td>
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$^a$From ref. [9].

A tetragonal phase is formed, where the $c$ parameter is roughly five-times the $a$ parameter. This corresponds to the five layered perovskite reported earlier [7,8] where there is an ordering of Cu and Ti ions along the $c$-axis. It is seen that there is an increase in the lattice parameter with increase in zinc substitution from $a = 3.91308\pm \text{Å}$ and $c = 19.6301\pm \text{Å}$ at $x = 0$ to $a = 3.925\pm \text{Å}$ and $c = 19.64\pm \text{Å}$ for $x = 1$. This is expected as Zn$^{2+}$ has a greater ionic radius than Cu$^{2+}$. However, in case of the zinc-rich phases ($x = 1.5$ and 2.0), the ordering is destroyed and these compounds are found to stabilize in a disordered (cubic) structure with $a = 3.933\pm \text{Å}$ and $3.937(1)\pm \text{Å}$ for $x = 1.5$ and 2.0, respectively. The refined lattice parameters for the different compositions are given in Table 1. The synthesis and structural characterization of the pure Zn composition ($x = 2$) has been carried out earlier [9] using powder X-ray, neutron and electron diffraction. The lattice parameter obtained from neutron diffraction was $a = 3.94263\pm \text{Å}$ [9]. In earlier reports [7,8] of related copper based ordered oxides, the copper layers were made of corner-shared CuO$_5$ square-pyramidal units. The probability of having zinc in such a coordination is unusual, since Zn prefers a tetrahedral or octahedral coordination. This may be an important factor in the stability of the disordered perovskite structure, as seen in all the pure Zn based compositions ($\text{Ln}_2\text{Ba}_2\text{CaZn}_2\text{Ti}_3\text{O}_{14}$; $\text{Ln} = \text{La, Nd, Pr}$) [9,10] reported by us. This is also observed in the zinc rich phases studied here. Attempts to promote ordering by annealing at temperatures varying from 700 to 950 °C for several days followed by slow cooling have not yet resulted in any ordering of the cations in the Zn-rich ($x > 1$) compositions. The La-Cu based oxides [8] ($\text{La}_2\text{Ba}_2\text{CaCu}_2\text{Ti}_3\text{O}_{14}$) have also been found to have the cubic perovskite structure.

We have also synthesized the above oxides of composition Nd$_2$Ba$_2$CaCu$_{2-x}$Zn$_x$Ti$_3$O$_{14}$ by the polymeric citrate precursor method. The X-ray diffraction patterns of the compounds after heating at 800 °C can be indexed on a cubic cell with $a = 3.91501\pm \text{Å}$ for $x = 0$, and $a = 3.94601\pm \text{Å}$ for $x = 2$ composition (Fig. 2). Note that all the oxides crystallize in the cubic structure. Thus, the cation ordering is destroyed when alternative low temperature synthetic routes have been employed since even the copper-rich phases (which are tetragonal when synthesized by the ceramic route) get stabilized in the cubic structure when prepared by the citrate precursor route.

The scanning electron micrographs for the compositions with $x = 0$, 1.0, and 2.0 (prepared by the ceramic method) have been obtained from the disks compacted at 4 tonnes pressure and sintered at 1200 °C. It is seen that the materials are highly dense. There is an increase in grain size with increase in zinc substitution. The grain size for $x = 0$ is around 2 mm (Fig. 3(a)), for $x = 1.0$ it is 3 mm (Fig. 3(b)) and for $x = 2.0$ it is as high as 7 mm [9]. It is seen that with increase in zinc substitution there is loss of well faceted boundaries. This could be due to the partial melting of grains of zinc containing...
compounds at the high temperature of around 1200 °C (zinc containing compounds are expected to have low melting points compared to those of copper). The grain size obtained by the citrate route (for samples sintered at 1000 °C) was lower and was around 0.5-1 mm for the pure copper composition (Fig. 4(a)) and around 1-2 mm for the pure Zn composition (Fig. 4(b)). Thus, the grain size increases with Zn content, as is the case for the oxides prepared by the ceramic route. There is a high degree of agglomeration of the grains in case of the composition with \( x = 0 \). It is also found that the grains are nearly spherical and do not show the morphology of the oxides prepared by the ceramic route. There is no sign of partial melting in the oxides prepared by the citrate route (after 1000 °C sintering).

The dielectric properties of the entire family of oxides \( 0 < x < 2 \) have been studied for oxides prepared by the ceramic and the citrate precursor routes. The variation of dielectric constant (\( \varepsilon \)) and dielectric loss (\( D \)) with composition at room temperature at 500 kHz is shown in Fig. 5. It is observed that the room temperature dielectric constant (\( \varepsilon \)) shows a slow increase as \( x \) increases from \( x = 0 \) (\( \varepsilon = 8 \)) to 1.5 (\( \varepsilon = 11 \)), beyond which it shows a very sharp rise and rises to around 60 for \( x = 2 \). Thus, there is a tremendous rise in dielectric constant with decrease in Cu content beyond \( x = 1.5 \) (Fig. 5). The oxide \( \text{Nd}_2\text{Ba}_2\text{CaZn}_2\text{Ti}_3\text{O}_{14} \) \( (x = 2) \) has been reported [9] to have a dielectric constant (\( \varepsilon \)) of 59 and dielectric loss of 0.0047 at room temperature at 100 kHz. Though the dielectric constant of the pure copper phase is very low (\( \varepsilon = 8 \)), the two probe resistivity for all the phases show high resistance of the order of megaohms. We would normally expect that Cu-rich compositions should show much lower resistivity, which would lead to low dielectric constant. However, there is no appreciable fall in the resistivity and even the pure copper compositions shows resistivity in the megaohms range. The dielectric loss of the above oxides decreases from about 0.05 \( (x = 0) \) to 0.005 \( (x = 2) \) (Fig. 5). The dielectric constant (\( \varepsilon \)) for the composition \( (x = 1) \) was found to be around 9.5 at 100 kHz at room temperature. The dielectric constant and dielectric loss showed nearly constant values in the range of 3-500 kHz (Fig. 6). The dielectric loss was 0.06 at the same frequency and temperature and decreased to around 0.03 at 500 kHz (Fig. 6). The dielectric constant also remains quite stable (around 9) with temperature (inset of Fig. 6) and the temperature coefficient of the dielectric constant is
Fig. 3. Scanning electron micrographs of Nd$_2$Ba$_2$Ca$_2$Zn$_2$Ti$_3$O$_{14}$: (a) $x = 0$ and (b) $x = 1$ prepared by the ceramic route.

found to be $1 \times 10^{-4} \, ^\circ\text{C}^{-1}$. For the $x = 1.5$ compound at 500 kHz and at room temperature the dielectric constant ($\varepsilon$) and has a value of 11 (Fig. 7) and is found to be highly stable over a large frequency range, from 250 Hz to 500 kHz as seen in Fig. 7. The dielectric loss is stable around 0.01 in the frequency range of 50-500 kHz. This compound shows a large increase in $\varepsilon$ values with change in temperature beyond 150 $^\circ\text{C}$ (inset of Fig. 7). Similar behavior is also observed for the dielectric loss, which is quite stable over a large range of frequencies (and at temperatures <150 $^\circ\text{C}$).

The dielectric properties of the oxides prepared by the citrate precursor route and sintered at 1000 $^\circ\text{C}$ have also been studied. It is found that there is a decrease of dielectric constant ($\varepsilon$) of all the compounds when prepared by the citrate precursor method. The dielectric constant ($\varepsilon$) for the oxide Nd$_2$Ba$_2$CaZn$_2$Ti$_3$O$_{14}$ ($x = 2$) has a value of 23, when prepared by the citrate method. This oxide prepared by the ceramic route shows a high dielectric constant of 59 [9]. However, the stability of the dielectric constant with frequency in the range 10-500 kHz is not affected by the method of synthesis (Fig. 8). The dielectric loss is around 0.007 at room temperature and reduces to 0.005 at 300 $^\circ\text{C}$ at 100 kHz. Note that this oxide had a dielectric loss of 0.0047 when prepared by the ceramic route [9].
Fig. 4. Scanning electron micrographs of Nd$_2$Ba$_2$Ca$_{2-x}$Zn$_x$Ti$_3$O$_{14}$: (a) $x = 0$ and (b) $x = 2.0$ prepared by the citrate precursor route.

Fig. 5. Plot of variation of dielectric constant ($\varepsilon$) and dielectric loss (D) of Nd$_2$Ba$_2$Ca$_{2-x}$Zn$_x$Ti$_3$O$_{14}$ with composition ($x$) at room temperature at 500 kHz.
Fig. 6. Plot of variation of dielectric constant (ε) and dielectric loss (D) with frequency at room temperature for Nd$_2$Ba$_2$CaCuZnTi$_3$O$_{14}$ prepared by the ceramic route. Inset shows the variation of dielectric constant with temperature at 100 kHz.

Fig. 7. Plot of variation of dielectric constant (ε) and dielectric loss (D) with frequency at room temperature for Nd$_2$Ba$_2$CaCu$_{0.5}$Zn$_{0.5}$Ti$_3$O$_{14}$ prepared by the ceramic route. Inset shows the variation of dielectric constant with temperature at 100 kHz.

Fig. 8. Plot of variation of dielectric constant (ε) and dielectric loss (D) with frequency at room temperature for Nd$_2$Ba$_2$CaZn$_3$Ti$_3$O$_{14}$ prepared by the citrate precursor route. Inset shows the variation of dielectric constant with temperature at 100 kHz.
The dielectric constant in this case shows a very marginal decrease with temperature and varies from 23 at room temperature (around 35 °C) to 21 at 300 °C at 100 kHz (inset of Fig. 8). Note that for the Zn rich composition \(x = 1.5\) (Fig. 7) the dielectric constant shows an increase and for \(x = 2\) [9], the dielectric constant increases from 59 to 63 at temperatures greater than 150 °C. The dielectric constant \(\varepsilon\) for the oxide with composition \(x = 0\) is around 7 and the loss is around 0.03 at room temperature at 100 kHz. Thus, for the pure Cu phase \(x = 0\) there is not much change in the dielectric constant by the synthetic route. The higher dielectric constant in case of the samples prepared by the ceramic route could be due to two reasons: first the density of pellets prepared by the citrate route (92%) was found to be marginally lower than those obtained by the ceramic route (93-95%). This lower density probably affects the dielectric constant as is known from earlier studies [15]. Secondly, the grain sizes obtained for the particles prepared by the citrate route are lower than those obtained by the ceramic route. This is especially seen for the Zn-rich phases where grain sizes are 7 mm for the ceramic route compound to 1-2 mm for the oxide obtained by the citrate precursor route. Smaller grains normally lead to increase in grain boundaries. This means that the short-range migration of charges which occur along the grain boundaries will be affected by the change in grain size and in turn lead to the decrease in the dielectric constant. Such effects of grain size on the dielectric constant has been reported earlier [16].

4. Conclusion

It has been found that solid solutions of zinc and copper based on the formula \(\text{Nd}_2\text{Ba}_2\text{Ca}_{2-x}\text{Zn}_x\text{Ti}_3\text{O}_{14}\) has been successfully prepared for the entire range of composition. The oxides show a tetragonal to cubic transition at high content of Zn. The citrate precursor route leads to monophasic oxides at much lower temperatures where all the oxides could be indexed on a cubic cell. The dielectric constant varies marginally with composition (8-11) for \(0 < x < 1.5\) and is much higher for the pure Zn composition \(x = 2\). Most of these oxides show highly stable dielectric properties with frequency. Though monophasic oxides are afforded by the low temperature citrate precursor route, the lower grain size of these oxides leads to lower dielectric constant. The oxides of the formula \(\text{Nd}_2\text{Ba}_2\text{Ca}_{2-x}\text{Zn}_x\text{Ti}_3\text{O}_{14}\) provide for a family of materials with tunable dielectric properties and having nearly the same basal lattice parameter, which renders them to be exploited for designing novel multilayer capacitors.

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